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ON THE ASSIGNMENT OF SOME VIBRATION FREQUENCIES OF A FEW SUBSTITUTED BENZENES

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ABSTRACT. From a comparison of the relative strengths of infra red bands and relative intensities and values of factors of depolarisation of certain Raman lines of a few mono- and disubstituted benzenes it has been concluded that it is possible to remove some difficulties in certain assignments proposed by previous workers by revising some of those assignments. The frequencies of vibrations corresponding to ν_1, ν_6, ν_8, ν_{12} and ν_{19} of benzene have been dealt with in detail in the cases of a few substituted benzenes. It has been suggested that in substituted benzenes the degeneracy of ν_8 and ν_{19} is split up owing to the displacement of the C-X groups as single masses during the vibrations. The frequencies of modes 8A and 19A have been identified in certain cases.

INTRODUCTION

The assignments of frequencies of a large number of mono- and disubstituted benzenes have been made by many previous workers, but in most of the cases the assignment has been made on the basis of the frequencies observed either in the Raman spectra or in the infra red spectra. A detailed discussion of the probable modes giving the different frequencies of some monosubstituted benzenes was, however, made by Whiffen (1956) taking into consideration both the infra red and Raman spectra of these compounds. Fuson *et al* (1960) studied the infra red spectra of toluene, toluene-d_8 and toluene-d_3 and from a comparison of the frequencies of the three compounds observed in the infra red spectra they assigned most of these frequencies to suitable modes. The infra red spectra of halogen substituted benzenes in the vapour and liquid states were studied recently by Sirkar *et al* (1964) and those of parafluorotoluene and the chlorotoluenes in the two states were studied by Mukherjee *et al* (1965) and it was found that alternative assignments of some of the frequencies were possible. A survey of the Raman and infra red spectra of mono- and disubstituted benzenes was therefore made and the relative intensities of the Raman lines and corresponding infrared bands as well as the polarisation of the Raman lines seemed to corroborate the view expressed

above. It is the purpose of the present paper to point out difficulties about the assignments proposed by previous workers and to discuss the alternative assignments which are possible in the cases of some of the frequencies of a few mono- and disubstituted benzenes.

MONOSUBSTITUTED BENZENES

As pointed out by previous authors the Raman spectra of toluene and halobenzenes show a strong polarised line at about 1000 cm^{-1} and another such line of slightly higher frequency-shift. The first line is observed also in the Raman spectra of all metadisubstituted and symmetrical trisubstituted benzenes, and therefore, it has been rightly assigned to the breathing mode of the benzene ring symmetrical to the three fold axis in which only the carbon atoms at positions 2, 4 and 6 are displaced radially while the other three atoms of the ring remain at rest. This mode is different from ν_{12} and it has been shown as mode '*p*' by Whiffen (1956). There are also two more strong lines in the neighbourhood of this line in the Raman spectra of all monosubstituted benzenes. The first of these two lines has the Raman frequency 1027, 1025, 1021, 1023, 1019 and 1023 cm^{-1} (Magat, 1936) in the case of toluene, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene and benzonitrile respectively. The factor of depolarisation of this line is slightly higher than that of the line due to the '*p*' mode mentioned above. There is also a fairly strong band of this frequency in the infra red spectra of these substances. This line has been assigned to ν_{18A} by previous workers, but this C–H vibration should be inactive in the Raman effect. Hence it would be desirable to find out another mode which would give a strong and highly polarised Raman line as well as a strong infrared band. Such a mode is shown in fig. 1(a). In this case

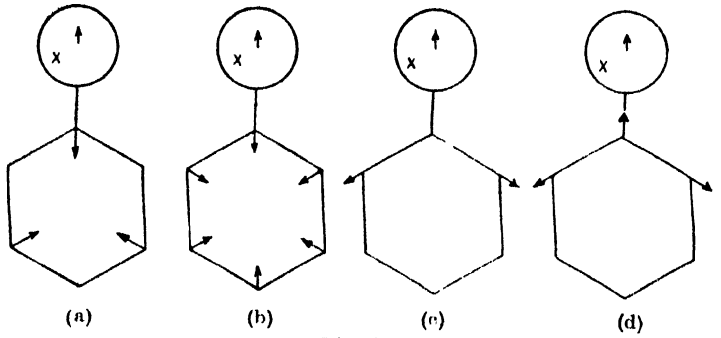

Fig. 1.

the carbon atoms 1, 3 and 5 move radially and the other three carbon atoms are at rest while there is stretching of the C–X bond. Such an assignment is supported by the fact that paradisubstituted benzenes do not give this line. The other line mentioned above is of slightly higher frequency-shift which has the value about

1085 cm^{-1} in the case of chlorobenzene and the factor of depolarisation of this line is slightly larger than that of the line due to mode '*p*' mentioned above. This line has been assigned by Whiffen (1956) to a mode called '*q*' in which there is breathing of the ring with stretching of the C–X bond as shown in fig. 1(b). Thus just like splitting of ν_1 into two modes in one of which the C–X bond remains unaltered and in the other it is stretched, ν_{12} is also assumed to be spilt up into two modes in the assignment of the line 1021 cm^{-1} of chlorobenzene mentioned above.

As regards the assignment of the strong polarised line 806 cm^{-1} of fluorobenzene and similar other lines of chloro-, bromo- and iodobenzene it has to be pointed out that there is also a very strong band at 805 cm^{-1} in the infrared spectrum of fluorobenzene and the factor of depolarisation of this Raman line is 0.5. It is unlikely that the breathing vibration without C–F streching will have such large factor of depolarisation. In this particular case probably C–F stretching oscillation is responsible for both the Raman line and the band at 806 cm^{-1}. In the cases of the heavier substituents like Cl, Br. and I the asymmetry introduced during the breathing vibration may be responsible for the infra red band, because in the case of chlorobenzene the factor of depolarisation of the line 700 cm^{-1} due to such vibration is only 0.13.

In the Raman spectra of toluene and all other CH_3-substituted benzene compounds there is a strong and polarised line at about 1210 cm^{-1}. In the case of toluene the corresponding infra red band is very weak. While discussing the infrared frequencies of toluene, Fuson *et al* (1960) have not assigned the weak band at 1210 cm^{-1}. Such a weak band also appears in the infra red spectrum of *p*-chlorotoluene (Sirkar *et al*, 1965). Evidently, the vibration giving the strong line is almost inactive in the infra red. This line can not be assigned to any vibration of the CH_3 group because a weak band appears even in the infra red spectrum of toluene-d_8 (Fuson *et al*, 1960) and some other molecules like CH_3Cl, C_2H_5Cl etc. do not give any strong Raman line at 1210 cm^{-1}. A localised oscillation in which the three adjacent carbon atoms move against the central atom involving stretching of the C-C bonds as shown in fig. 1(c) might be responsible for the line in the neighbourhood of 1210 cm^{-1} mentioned above. As the C-C bonds are at 120° with each other the mode shown in fig. 1(c) would be inactive in the infra red. The two C-C bonds of the ring being involved in the stretching, the frequency of the oscillation is expected to be higher than that due to ordinary C-C stretching.

The Raman line 1220 cm^{-1} of fluorobenzene is moderately intense and its factor of depolarisation is 0.5 (Magat, 1935). The infra red band of this frequency is, however, extremely strong and therefore the corresponding vibration must be highly asymmetric. The oscillation similar to that giving the line 1210 cm^{-1} of toluene mentioned above is not expected to produce such an intense infra red

band and probably an asymmetric mode of the ring is responsible for this strong infra red band. Also ν_{12} combined with C-F stretching may not be responsible for this band, because the frequency is too high and ν_{12} being forbidden in the case of benzene it can not produce such an intense band in this case. Probably a localised oscillation in which the C-F group jointly moves as a single mass and the symmetrical C-C stretching takes place as shown in fig. 1(d) is responsible for this band. Such a motion takes place also in the upper half of the molecule in ν_{19A}, but in the vibration suggested here the lower half is assumed to remain stationary. Such a mode is active both in the infra red and in the Raman effect.

There is another apparent anomaly regarding the strengths of the infra red bands corresponding to the Raman lines 1002 and 1001 cm^{-1} of bromobenzene and iodobenzene respectively. The mode symmetric to the three-fold axis designated as '*p*' by Whiffen (1956) should be inactive in the infra red, but the corresponding bands in the infra red spectra of bromobenzene and iodobenzene are very strong, although they are weak in the infra red spectra of toluene, fluorobenzene and chlorobenzene. Probably, some other asymmetric mode has accidently a frequency in the neighbourhood of the frequency in these three cases. The frequency of mode 18A of benzene may have a slightly lower value in these monosubstiuted benzenes and the band near 1000 cm^{-1} may be due to 18A.

DISUBSTITUTED BENZENES

Although most of the authors who have reported the Raman and infra red spectra of disubstituted benzenes have also suggested some assignments of the observed frequencies, such assignments of the frequencies of symmetrical and unsymmetrical parahalogen-substituted benzenes suggested by Stojiljkovic and Whiffen (1958) are based on a comparative and exhaustive study of both the infra red and the Raman spectra of the compounds and these assignments have been adopted also by many later authors (Scherrer *et al*, 1963; Shurvell *et al*, 1966). As some of the assignments of the parasubstituted compounds are also related to a few such assignments in the cases of the ortho-and meta-substituted compounds it is proposed to discuss first some probable alternative assignments in the cases of the para substituted benzenes dealt with by previous workers.

Among the vibrations of the class a_g there is one giving strong polarised Raman lines 330, 214 and 157 cm^{-1} in the spectra of *p*-dichloro-, *p*-dibromo-and *p*-diiodobenzene respectively. This frequency has been assigned by Stojiljkovic and Whiffen (S. & W) (1958) to a mode involving X-R-X stretching in which R represents the ring. Scherrer and Evans (1963) have also agreed with S. & W. and have found the value of the force constant for C-Cl stretching to be 1.986×10^5 dynes/cm, which is rather too low. It is also doubtful whether the C-Cl bending frequency (351 cm^{-1}) can be higher than C-Cl stretching frequency as assumed by S. & W (1958). On the other hand, the Raman line 747 cm^{-1} of *p*-dichlorobenzene

has been assigned by them to a mode similar to the mode 6A (Pitzer *et al*, 1943) of benzene, although in mode no.5 given by S & W (1958) no displacement of the carbon atoms 1 and 4 has been shown. They have not explained why this frequency should be higher in this cases than in benzene. In the Raman spectra of chloro-, bromo- and iodobenzene also there are lines at 418, 316 and 268 cm^{-1} respectively similar to the lines 330, 214 and 157 cm^{-1} respectively of the para-substituted benzenes. As pointed out earlier, the approximate C-X stretching vibration in fluoro-,chloro- and bromobenzene may have frequencies near 806, 700 and 673 cm^{-1} respectively, and therefore, the above lower frequencies of these molecules are to be assigned to some other symmetric mode. Probably, in the mode similar to 6A of benzene the substituent moves in phase with the adjacent carbon atom and in that case the frequency is expected to be lower than 606 cm^{-1}. If in chlorobenzene it is lowered from 606 cm^{-1} to 418 cm^{-1} it is quite likely that in para-dichlorobenzene it is still further lowered to 330 cm^{-1}. So this latter frequency is to be assigned preferably to a mode similar to 6A of benzene on the assumption that the two substituents move in phase with the carbon atoms to which they are attached. Such an assumption is justified by the facts that the value of ν_{6B} even of *m*-dichlorobenzene is much lower than that of *p*-dichlorobenzene and that the frequencies ν_1 and ν_6 of C_6D_6 are lower than those of C_6H_6.

The conclusion about the mode of 6B of *m*-dichlorobenzene is drawn from a comparison of the Raman spectrum of this compound with that of 1,3, 5-trichlorobenzene. If both these molecules are assumed to belong to space group C_{2v} the frequency of the vibration similar to mode 6B of benzene is expected to be the same in both these cases and the Raman line due to such a vibration is expected to be depolarised and of the same intensity in both the cases. In the Raman spectrum of *m*-dichlorobenzene reported by Sponer and Kirby-smith (1941) only the line 428 cm^{-1} has a factor of depolarisation greater than 0.5, while the value for the line 666 cm^{-1} is 0.25. There is also a strong infra red band at 672 cm^{-1} in the infra red spectrum of this compound (Scherrer et al, 1963). The line 428 cm^{-1} is more suitable for the mode 6B than the line 666 cm^{-1}, because 1, 3, 5-trichlorobenzene also gives a Raman line at 428 cm^{-1} and it does not show any Raman line in the neighbourhood of 650 cm^{-1}. Also the line due to 6B can not have a factor of depolarisation as low as 0.25 and a small stretching of the C-Cl bonds in 6B assumed by Scherrer (1963) is not expected to produce such a strong infra red band at 672 cm^{-1} mentioned above. The frequency of vibration 6A of *m*-dichlorobenzene is expected to be slightly higher than that of 1, 3, 5-trichlorobenzene and probably the lines 375 cm^{-1} of the latter molecule and 399 cm^{-1} of *m*-dichlorobenzene are due to this mode. Hence the assignment of a very weak Raman line with a frequencyshift larger than 666 cm^{-1} to 6A in the case of *m*-dichlorobenzene is not quite satisfactory.

Before discussing the assignments of the lines 658, 666 and 747 cm^{-1} of ortho-, meta and *p*-dichlorobenzene necessitated by the assignment of modes 6A and 6B

indicated above, it would be worthwhile to identify the modes giving the line 1126 cm^{-1} of *m*-dichlorobenzne. The factor of depolaristion of this line is 0.1. There is also a strong infra red band at 1129 cm^{-1} in this case while in the case of 1, 3, 5-trichlorobenzene there is no infra red band corresponding to similar intense line 1146 cm^{-1} (Scherrer *et al*, 1962). Hence in the latter case the oscillation giving this line is symmetrical with respect to the three-fold axis. The line 1126 cm^{-1} of *m*-dichlorobenzene can not be assigned to 9A, because in the case of *o* dichlorobenzene also there is such a line at 1129 cm^{-1} and an infra red band of the same frequency which shifts only to 1065 cm^{-1} when the four hydrogen atoms are substituted by deuterium atoms (Scherrer *et al*, 1963). The low value of the factor of depolarisation of the line 1126 cm^{-1} suggests that the line is due to the symmetric breathing vibration of the ring in which there is slight stretching of the C-Cl bonds giving rise to the infra red bands. In the case of 1, 3, 5-trichlorobenzene the three C-Cl bonds being at 120° with each other such a simultaneous stretching of the three bonds is inactive in the infra red. As the line 399 cm^{-1} of *m*-dichlorobenzene has a factor of depolarisation as low as 0.1 it is also due to such a symmetrical vibration in which the two C-Cl groups move as single masses as suggested above. The line 399 cm^{-1} of *m*-dichlorobenzene can not be assigned to C-Cl stretching vibration because in that case the factor of depolarisation of the line would be higher than that of the line 1126 cm^{-1}. These facts clearly indicate that the frequency of C-Cl stretching oscillation in substituted benzenes is higher than 400 cm^{-1}.

In the case of 1, 2, 4-trisubstituted benzenes also there are two lines in this region between 300 cm^{-1} and 500 cm^{-1}. For instance, in the case of 2, 4-dichlorobenzyl chloride there are two polarised lines at 461 cm^{-1} 332 cm^{-1} respectively (Deb, 1963). Similarly, 1, 2, 4-trichlorobenzene also shows two lines at 459 cm^{-1} and 332 cm^{-1} respectively (Deb and Banerjee, 1960). If an axis passing through positions 1 and 4 is assumed to exist in the case of the ring the frequency of mode 6B in these cases is expected to be higher than that of *m*-dichlorobenzene, while the frequency of mode 6A is expected to be lower. So, the first of these two frequencies in each of these two cases is to be assigned to 6B and the second to 6A. The frequencies of these two oscillations in 3,4-dichlorobenzyl chloride are also expected to be the same as those in 2, 4-dichlorobenzyl chloride and actually, there are two strong lines at 464 and 333 cm^{-1} in the Raman spectrum of 3, 4-dichlorobenzyl chloride (Deb, 1963).

As regards the line 658 cm^{-1} of *o*-chlorobenzene it is to be pointed out that the corresponding infra red band is moderately strong and the factor of deapolarisation of this line is not as low as that of the line 1129 cm^{-1} mentioned earlier. Also the infra red band 660 cm^{-1} shifts to 630 cm^{-1} with the substitution of the hydrogen atoms by deuterium atoms (Scherrer *et al*, 1963). Hence the masses of the deuterium atoms have slight influence on the frequency of the vibration giving the line. Probably the breathing vibration in which the two C-Cl groups move as

single masses gives rise to this line. The assymetry of the molecule may be responsible for the appearance of the infra red band. The same oscillation may also produce the line 666 cm^{-1} of *m*-dichlorobenzene. On such an assumption a similar mode in 1, 2, 3-trichlorobenzene is expected to have a much lower frequency and actually there is an intense polarised line 516 cm^{-1} in the Raman spectrum of this compound (Scherrer *et al*, 1963). So, in these molecules with substitution only on one side of the centre the breathing vibration appears to take place in the two ways mentioned above.

The line 742 cm^{-1} of *p*-dichlorobenzene is due to a vibration of a_g type. If it is alternatively assigned to mode 1 instead of mode 6A owing to its large intensity it has to be assumed that the two C-Cl groups move as single masses. The influence of such heavier masses at positions 1 and 4 is clealy indicated by the diminution of the frequency from 992 cm^{-1} to 858 cm^{-1} and 747 cm^{-1} in the cases of fluoro- and chlorobenzene respectively but such an influence is not clearly indicated in the case of *p*-dibromo and *p*-diiodobenzene, because the frequencies diminish only to 709 cm^{-1} and 686 cm^{-1} respectively in these two cases. It is, therefore necessary first to justify the assignment of the line 747 cm^{-1} of *p*-dichloro-

Table 1

Raman frequencies in cm^{-1}

C_6H_6 Herzberg (1945)	C_6D_6 Herzberg (1945)	*p*-Dichloro benzene S and W (1958)	*p*-Dichloro benzene-d_4 Scherrer and Evans (1963)	C_6Cl_6 Scherrer and Evans (1963)
			226 (6)D*	219 (37) D
		299 (8) D	289 (38)D	
		330 (12) P	328 (100) P	323 (47) D
	337 (w)	351 (3) D		340 (10)
404 (w)				372 (100) P
	576.7 (1.2)D			
605 (2.1) D		628 (8) D	609 (37) D	
			632 (13)D*	
		747 (12) P	713 (51) P	
848.9 (0.9) D	661.2 (1.4) D	811 ($\frac{1}{2}$) D	724 (36) P*	
			867 (46) P	
991.6 (10.0) P	944.7 (10) P	1069	1051 (27) P*	
1030 (w)		1087 (8) P		
		1106 (12) P	1082 (93) P	1170 (5)
1178 (2.2) D	867.2 (2.3)D	1169 (5) P		1187 (17) P
		1233 ($\frac{1}{2}$)		
		1248 D		1222 (30) P
		1248 D		
	1327 w	1291 (3)		
1584.8 (1.9)D	1558.6 (2)D	1378 (1) D		1420 (3)
1606.4 (1.6)D		1485 D	1531 (20) D	1512 (24) D
		1573 (12) D	1558 (73) D	
		1632 ($\frac{1}{2}$)		
3046.8 (4.8) D	2263.9 (6.1) D		2281 (29) D	
3061.9 (10.6) P	2292.3 (10.6) P	3072 (1)	2299 (64) P	

*Saeki (1962) did not observe these lines of *p*-dichlorobenzene-d_4

benzene to mode 1 and then to find out the cause of the anomaly mentioned above. For this purpose the prominent Raman frequencies of benzene, benzene-d_6, *p*-dichlorobenzene, *p*-dichlorobenzene-d_4 and hexachlorobenzene are compared in table 1.

It can be seen from table 1 that the value of ν_6 of benzene diminishes from about 606 cm^{-1} to 577 cm^{-1} with the substitution of the six hydrogen atoms by deuterium atoms while for the same substitution the value of ν_1 diminishes from 992 cm^{-1} to 945 cm^{-1}. Hence the change due to the influence of the deuterium atoms in the case of ν_1 is 47 cm^{-1} while that in the case of ν_6 is 29 cm^{-1}. In the case of *p*-dichlorobenzene the value of ν_{6B} is 628 cm^{-1} and it diminishes to 609 cm^{-1} with the substitution of four hydrogen atoms with deuterium atoms. This change by 19 cm^{-1} is consistent with that observed with benzene, because when all the six hydrogen atoms of benzene are substituted the change is 29 cm^{-1}. The line 747 cm^{-1}, however, shifts to 713 cm^{-1} with the substitution and thus the frequency changes by 34 cm^{-1}. Such a change is consistent with the change in ν_1 in the case of benzene and it is too large in comparison with the change for ν_6, because there are only four deuterium atoms in this case. Hence these spectra clearly indicate that the line 747 cm^{-1} of *p*-dichlorobenzene is to be assigned to ν_1 in which the C-Cl groups move as single masses.

As regards the unexpectedly large values of the corresponding frequencies in the cases of *p*-dibromo- and *p*-diiodobenzene it might be possible that owing to much heavier masses at positions 1 and 4 in these two cases, the displacements of the C-X groups as single masses are much smaller than those of the remaining four carbon atoms of the ring. Such an oscillation is not exactly symmetric to the six-fold axis but it is of a_g type.

Columns 3 and 4 of table 1 further show that the strong line 1106 cm^{-1} of *p*-dichlorobenzene shifts to 1082 cm^{-1} when the four hydrogen atoms are substituted by deuterium atoms. This change in the frequency is 24 cm^{-1} and it is much smaller than that expected for ν_1 from the comparison of the values of ν_1 of benzene and benzene-d_6. This fact probably indicates that the line is due to a vibration in which the carbon atoms move almost at right angles to the C-D bonds. The only vibration of type a_g satisfying this condition is 8A. It may be possible that in 8A also the C-Cl groups in this case move as single masses giving rise to a line of frequency much lower than 1573 cm^{-1} which should be the frequency of the line due to 8B, because the influence of the masses of the chlorine atoms is very small in this latter mode. It is significant that although 8A is of type a_g, the line 1573 cm^{-1} is totally depolarised. This indicates that the line is due entirely to 8B and the line due to 8A has a different frequency. It is suggested here that when the substitutions are only in the positions 1 and 4, ν_1 is of one type in which there is no stretching of the C-Cl bonds and ν_{8A} and ν_{8B} have different frequencies owing to the influence of the masses of the substituents.

It would be of interest to compare the Raman frequencies of hexachlorobenzene given in column 5 of table 1 with those of *p*-dichlorobenzene. There are two intense and polarised lines 374 cm^{-1} and 1226 cm^{-1} respectively in the spectrum due to hexachlorobenzene. As pointed out earlier, the symmetric breathing vibration of 1, 2, 3-trichlorobenzene may have the frequency 516 cm^{-1} and when the remaining three hydrogen atoms are replaced by chlorine atoms this frequency should be lowered appreciably. Hence the line 372 cm^{-1} of hexachlorobenzene may be due to such breathing vibration in which the six C-Cl groups move as single masses. The line 1226 cm^{-1} may then be assigned to the breathing vibration in which there is stretching of all the C-Cl bonds. In fact this mode is the real breathing vibration of the ring because there is very little displacement of the Cl atoms. In the other case when the Cl atoms move outwards the lighter carbon atoms are dragged with them and instead of producing a C-Cl stretching oscillation such displacements produce another breathing vibration in which each of the C-Cl groups moves as a single mass. There is a third line at 1187 cm^{-1} which is weaker but polarised. Scherrer and Evans (1963) have assigned this line to a combination of two modes. It is to be pointed out, however, that the frequency ν_{8B} in this case is 1512 cm^{-1} which is smaller than that for benzene. Hence the influence of the mass of the substituent chlorine atoms on this frequency is clearly indicated by this lower value. There is also no line of frequency higher than 1512 cm^{-1} in this case, which indicates absence of C-Cl stretching. Hence the frequency of the mode 8A in which the influence of the masses of the substituents is much greater is expected to be much lower than 1512 cm^{-1}. In fact, only the influence of masses of the chlorine atoms at positions 1 and 4 is predominant in this mode. So, the frequency may be almost the same as that in the case of *p*-dichlorobenzene. The line 1187 cm^{-1} may therefore be due to 8A. Of course, this vibration is not symmetric to the six-fold axis and therefore the line due to it should have been totally depolarised, but as mentioned above, only the substituents at the para positions determine the frequency of this mode, and therefore, the two-fold axis is probably the main element of symmetry which determines the polarisation of the Raman line produced by this mode.

As regards the vibration ν_6 of type e_{2g} the influence of the substituents should make the frequency lower in this case than that of *p*-dichlorobenzene. The corresponding Raman line should also be depolarised. The degeneracy is not expected to be split up because the displacements of the C-Cl groups are almost along the radii. The line 219 cm^{-1} of hexachlorobenzene can therefore be assigned to this mode.

ASYMMETRIC VIBRATIONS

There are two typical asymmetric vibrations of the benzene ring which do not appear in the Raman effect. These are ν_{12} and ν_{19}. The former mode is also inactive in the infra red because the three oscillating vectors are inclined at 120°

with each other. In the case of *p*-dichlorobenzene this mode is of type b_{1u} while 19A and 19B are of types b_{1u} and b_{2u} respectively. There is a band 1087 cm^{-1} in the infra red spectrum of this compound which is very very strong (Stojiljkovic *et al*, 1958) and it has been assigned to ν_{12}. There is also a fairly strong Raman line of the same frequency-shift which has been assigned by the above authors to the octave of a b_{1u} mode. As indicated above, ν_{12} is inactive in the case of benzene and has the value 1010 cm^{-1}. There is also a strong infra red band at 1015 cm^{-1} which has been assigned to υ_{18A} by those authors. The infra red spectrum of *p*-dichlorobenzene-d_4 reproduced by Scherrer and Evans (1963), however shows that this strong band persists even when the four hydrogen atoms are substituted by deuterium atoms. Hence this band can not be due to 18A but it may be due to ν_{12}. The spectrum further shows that the band 1087 cm^{-1} only shifts to 1020 $cm^{-1}$with the substitution of four hydrogen atoms. So this band is also due to an asymmetric vibration of the ring other than ν_{12}. The spectrum also shows that the 1478 cm^{-1} band shifts to 1365 cm^{-1} with the substitution mentioned above. Hence it is to be concluded that the band 1087 cm^{-1} may be due to ν_{19A} in which the C-Cl groups move as single masses. The Raman line 1087 cm^{-1} in this case may be due to a vibration in the upper half of the molecule as shown in fig. 1(d).

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